Contributions to the Chemistry of Boron, 228[◇]

Synthesis of Structures of (Acyloxy)boranes☆

Andreas Lang, Heinrich Nöth*, and Martin Schmidt

Institut für Anorganische Chemie der Universität München,
Meiserstraße 1, D-80333 München, Germany

Received February 15, 1995

Key Words: Trifluoroacyloxy-9-borabicyclo[3.3.1]nonane / Pivaloyloxy-9-borabicyclo[3.3.1]nonane dimer / Bis(9-borabicyclo[3.3.1]nonyl)oxalate / Tetrakis(9-borabicyclo[3.3.1]nonyl)-dihydroxyoxalate / Bis(9-borabicyclo[3.3.1]nonyl)-2,2-dimethylmalonate tetramer

9-Borabicyclo[3.3.1]nonane (9-BBNH) reacts with monocarboxylic acids to afford 9-(acyloxy)-9-borabicyclo[3.3.1]nonanes which are dimers in the solid state as shown by X-ray crystal structures of the benzoate and pivalate. More complex reactions were observed by allowing 9-BBNH to react with dicarboxylic acids in THF or monoglyme. Thus, $(9\text{-BBN})_2$ oxalate **3** contains a fully delocalized oxalate unit with equal C–O and B–O bond lengths. Traces of water convert it into the tetrakis(9-BBN) oxalate **5**. A rather unusual structure is veryfied by 9-BBN 2,2-dimethylmalonate **7** which according to its molecular structure is a tetramer featuring a 32-membered ring system. In contrast, reactions of oxalic acid with thexylborane leads to reduction of the acid and formation of a bicyclic dioxaborolo-dioxaborolane **10**. Several intermediates were detected by ^{11}B-NMR spectroscopy as well as in reactions of $BH_3 \cdot THF$ or $BH_3 \cdot SMe_2$ with oxalic acid. – It follows from the present study that (acyloxy)boranes derived from dicarboxylic acids are strong Lewis acids with an unexpected variety of structural features.

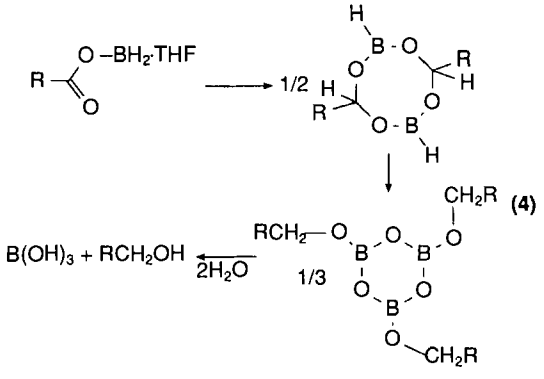
It is well-known that the carbon-boron bond of organoboranes is readily cleaved by carboxylic acids, a method used to determine the number of B–C bonds of organoboranes[2]. This method can be applied in a reverse manner to estimate the number of active protons, e.g. of carboxylic acids, by employing diethylborane as the reagent as shown by the elegant and systematic studies by Köster et al.[3]. Although it is evident that (acyloxy)boranes are formed in these reactions as the boron-containing products only a few compounds of this kind have been isolated and/or characterized so far[4]. For example, it was only recently that the product of the reaction of dimeric 9-borabicyclo[3.3.1]nonane, $(\mathbf{1})_2 = (9\text{-BBNH})_2$, with benzoic acid has been found to be a dimeric 9-(benzoyloxy)-9-BBN, featuring an eight-membered $B_2O_4C_2$ ring system[4]. On the other hand, $BH_3 \cdot THF$ (THF = tetrahydrofuran) reduces carboxylic acids rapidly to the corresponding alcohol[5,6] under mild conditions (0.5 h, 0–5 °C). Obviously, (acyloxy)boranes are intermediates in these reduction processes because Brown et al.[7] found a stepwise temperature-dependent H_2 evolution by studying reactions of pivalic acid with the borane-THF reagent as described by eqs. (1 to 3).

A bis(chloroacetoxy)borane was one of the characterized products obtained by the reaction between $BH_3 \cdot THF$ and $ClCH_2C(O)OH$, while $CF_3C(O)OBH_2 \cdot THF$ is stable in THF solution[7]. Reduction of the acyloxy group proceeds intermolecularly starting from mono(acyloxy)boranes via alkoxyboroxines as depicted in eq. (4). These results suggest that a study of (acyloxy)boranes would most likely lead to interesting results in terms of structures but would also be worthwhile in its own right in terms of association and reactions with Lewis bases[4]. In order to obtain results that are primarily determined by the acyloxy unit we selected the 9-BBN group with its rigid molecular framework which can also act as a probe for symmetry[8]. Consequently, most of the compounds reported here are (acyloxy)boranes derived from 9-borabicyclo[3.3.1]nonane.

$$Me_3C\text{-}C(O)\text{-}OH + BH_3 \xrightarrow[-70\,^\circ C]{THF} Me_3C\text{-}C(O)\text{-}O\text{-}BH_2 + H_2 \quad (1)$$

$$2\,Me_3C\text{-}C(O)\text{-}OH + BH_3 \xrightarrow[-40\,^\circ C]{THF} [Me_3C\text{-}C(O)\text{-}O]_2BH + 2\,H_2 \quad (2)$$

$$3\,Me_3C\text{-}C(O)\text{-}OH + BH_3 \xrightarrow[0\,^\circ C]{THF} [Me_3C(O)\text{-}O]_3B + 3\,H_2 \quad (3)$$



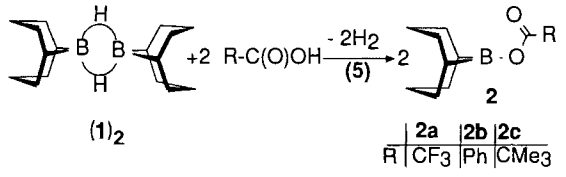
9-(Acyloxy)-9-borabicyclo[3.3.1]nonanes

We assumed that the acid strength as well as the space required by the group R of carboxylic acids RC(O)OH will

[◇] Part 227: Ref.[1].

  0009–2940/95/0808–0751 $ 10.00+.25/0

effect the structure of the (acyloxy)borane formed. Therefore, we treated a strong carboxylic acid, $CF_3C(O)OH$, one of medium acid strength, PhC(O)OH, and a comparatively weak one, pivalic acid, *t*BuC(O)OH, with the dimer of 9-BBNH, $(\mathbf{1})_2$. In each case, hydrogen evolution commenced quickly and was in most cases quantitative at 40°C as represented by eq. (5).

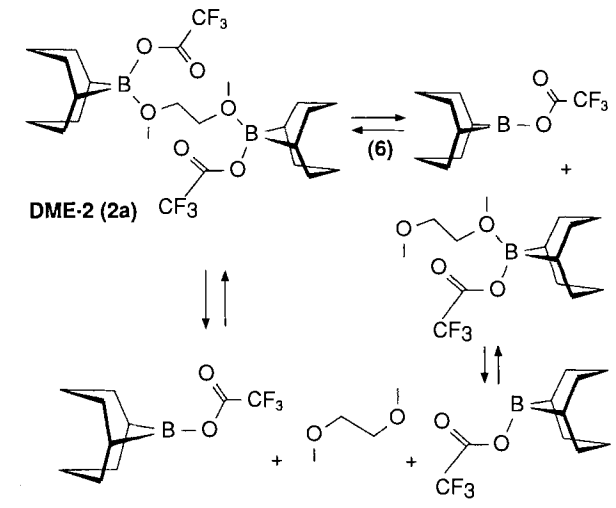


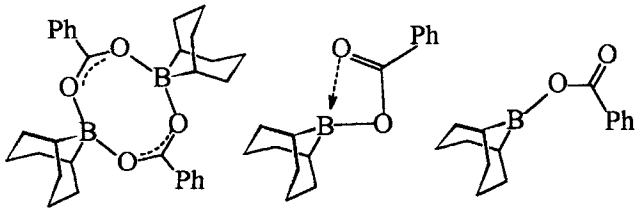
Compound **2a**, prepared in $CHCl_3$ solution, is a rather volatile, distillable liquid which fumes in air and seems to decompose slowly as it turns brown during storage even at −30°C. However, if the reaction is performed in dimethoxyethane the solvent adduct **2a** · **0.5 DME** can be isolated as a solid. This adduct sublimes unchanged at 50°C/0.05 Torr forming large crystals with dimensions of up to 1 cm. Attempts to determine its structure by X-ray methods failed because the crystals dissolved rapidly even in cold perfluoropolyether oil, and this prevented mounting them on the diffractometer in a cold stream. **2a** · **0.5 DME** is almost as prone to rapid hydrolysis as is **2a** itself.

The structures of compounds **2a** and **2a** · **0.5 DME** can be deduced from their NMR and IR spectra. The ^{11}B resonance of **2a** is compatible only with a tricoordinated boron atom, and $\delta^{11}B = 47.2$ is almost independent of the concentration of its solution in $CDCl_3$. There are three ^{13}C-NMR signals for the 9-BBN unit; thus, there must be free rotation about the B–O bond. On the other hand, the C=O stretching band is found at 1795 cm^{-1} which indicates a weak (if any) interaction of the carbonyl group with the boron atom. This interaction seems to be intramolecular since molecular mass determinations suggest the presence of a monomer in solutions. In contrast, the shielding of the ^{11}B nucleus of **2a** · **0.5 DME** in $CDCl_3$ solution is strongly concentration dependent, $\delta^{11}B = 55$ for a 0.01 M solution and $\delta = 47.2$ for a saturated solution. These data are in accordance with a dissoziation as shown in eq. (6), and similar observations were made by Köster et al.[4].

In DME solution the equilibrium (6) should be shifted to the left hand side, and $\delta^{11}B$ is found at 38.7. This chemical shift would still be in accordance with the presence of a tricoordinated boron atom, but the line width has become rather small and approaches those of tetracoordinated boron atoms. Therefore, we assume that exchange is still rapid, and the equilibrium lies not fully on the left hand side of eq. (6). Astonishingly, the ^{13}C-NMR signal for the CO group could not be detected in contrast to all other signals. Three ^{13}C-NMR signals for the 9-BBN unit (the boron-bound C atom is usually hard to detect) indicate free rotation about the B–O bond as also observed for **2a**.

Compound **2b** exhibits a rather broad ^{11}B-NMR signal at $\delta = 12.9$ in DMSO solution with a half width of 1230 Hz. This chemical shift suggests the presence of a compound with a tetracoordinated boron atom. However, we observed a significant dependence of $\delta^{11}B$ in $CDCl_3$ solution on concentraton (see also ref.[4]), and the signals found can be assigned to species **A** ($\delta = 3.6$), **B** ($\delta = 11.1$), and **C** ($\delta = 32.5$). This points to an equilibrium between monomeric and (most likely) dimeric molecules and would also be compatible with the rather large line width. Dimeric molecules of **2b** (= **A**) were observed for the solid (vide infra)[4].





A **B** **C**

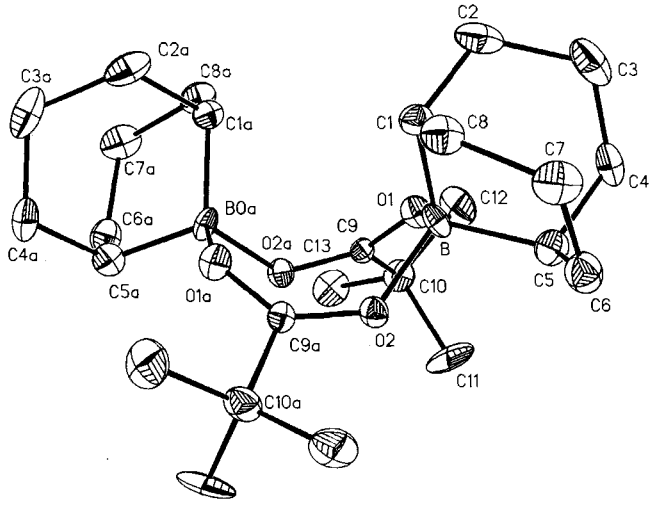
Compound **2c** is only sparingly soluble in $CDCl_3$, and, therefore, the ^{11}B-NMR spectrum was recorded in DME as solvent. $\delta = 22.6$ clearly indicates the presence of a tetracoordinated boron atom obviously due to DME addition to the boron atom because the IR bands observed for the RC(O)O function are also not compatible with a bidentate nature.

Due to unfavorable solubilities of **2b** and **2c** in benzene and cyclohexane their molecular masses could not be determined by cryoscopy, and mass spectra neither exhibit the parent peak for the monomer or dimer. However, masses higher than the monomer are abundant with a strong peak for $(9\text{-BBN})_2O^+$ as a characteristic ion, and even higher masses could be detected. This provides evidence that the compounds are at least dimeric. Since they crystallize well their structures in the solid state were determined by X-ray crystallography[9].

In contrast to **2b** which is dimeric and possesses a crystallographically imposed center of inversion for its eight-membered chair-shaped $B_2O_4C_2$ ring[4], we find a crystallogra-

phically imposed C_2 point-group symmetry for **2c** (the two-fold axis passes through the center of the eight-membered ring which shows a twisted boat conformation (see Figure 1). The B–O bonds are significantly different from one another while the two C–O bonds of the acyloxy groups differ only by 0.007 Å. Points worth mentioning are the rather large bond angles at the ring oxygen atoms, which are also observed in **2b** [B–O–C bond angle = 126.6(2)°] reflecting π-bonding to the carboxyl carbon atom. Taking the larger estimated standard deviations (esd values) for $(\mathbf{2c})_2$ into account, we have to consider the ring bond lengths and angles in the molecular structures of $(\mathbf{2b})_2$ and $(\mathbf{2c})_2$ as being almost equal. However, the B–O bonds are rather long compared with the B–O bonds in boric esters $B(OR)_3$[10] and $RB(OR)_2$[11] or $(RBO)_3$[10] compounds. Therefore, there is obviously little (if any) π-bonding contribution to the B–O bonds in contrast to the C–O bonds. Nevertheless, the eight-membered rings in the two compounds show different conformations. The "boat" conformation which results for the $B_2O_4C_2$ ring of $(\mathbf{2c})_2$ as compared to the chair-shaped ring of $(\mathbf{2b})_2$ originates obviously from the steric demand of the *t*Bu groups.

Figure 1. ORTEP-type representation of the molecular structure of **2c**. Thermal ellipsoids are shown on a 25% probability scale. Selected bond lengths [Å]: B–O1 1.572(7), B–O2 1.546(7), B–C1 1.578(9), B–C5 1.599(9), O1–C9 1.264(7), O2a–C9 1.257(7), C9–C10 1.516(7). – Selected bond angles [°]: O1–B–O2 106.2(4), O1–B–C1 114.7(5), O2–B–C1 113.6(4), O1–B–C5 106.2(4), O2–B–C5 107.5(5), C1–B–C5 108.3(5), B–O1–C9 133.0(4), B–O2–C9a 129.2(4), O1–C9–O2a 125.0(4)

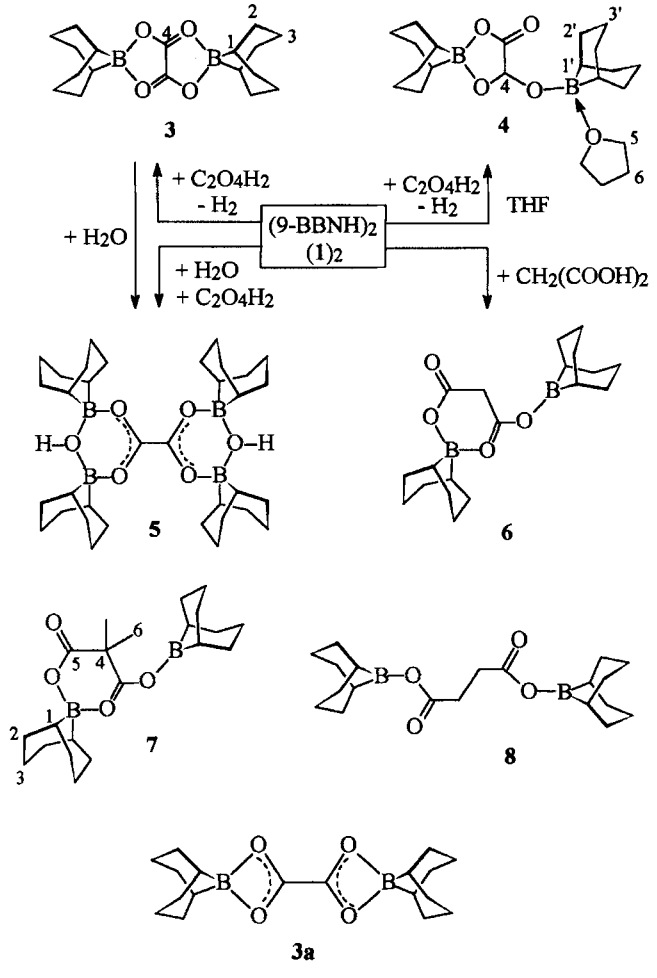


9-BBN-Derivatives of Dicarboxylic Acids

Reactions of $(\mathbf{1})_2$ with dicarboxylic acids may be more complex than with monocarboxylic acids since, apart from different stoichiometries, several coordination patterns may emerge. Our studies concentrated on 2:1 reactions of $(\mathbf{1})_2$ with oxalic acid, malonic acid, 2,2-dimethylmalonic acid, and succinic acid in DME as solvent. The use of THF as a solvent has to be avoided (vide infra) because it readily forms adducts with (acyloxy)boranes[4]. Hydrogen evolution sets in at about 0°C and is complete at 40–50°C whereby $(\mathbf{1})_2$ goes into solution. The products obtained under different conditions are shown in Scheme 1.

When $(\mathbf{1})_2$ is allowed to react with oxalic acid compound **3** is formed. However, if the reaction is performed in a DME/THF mixture compound **4** instead of the bis(9-BBN) oxalate **3** results. The coordinated THF in molecule **4** is not lost on crystallization from hot $CHCl_3$. Crystallization of **3** from boiling DME affords **5**. Obviously, hydrolysis has occurred as demonstrated by the almost quantitative formation of **5** from $(\mathbf{1})_2$, oxalic acid, and H_2O (ratio 2:1:2) in DME. In contrast, the formation of the carboxylates **6** to **8** proceeds in a straightforward manner. Compounds **3** to **5** are yellow in color, sparingly soluble in apolar solvents, but readily soluble in polar solvents such as DMSO or acetone. NMR and IR data (νCO) of these compounds are compiled in Table 1.

Scheme 1



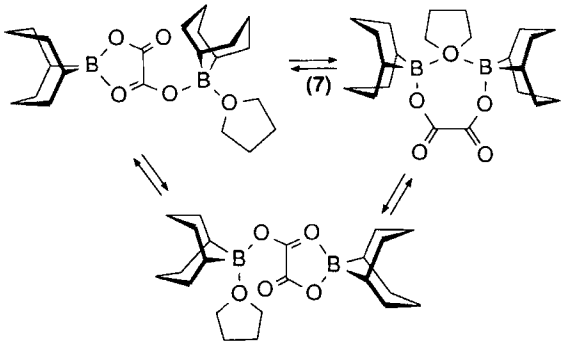
^{11}B-chemical shifts of the three boryl oxalates **3** to **5** indicate tetracoordination of their boron atoms. The boron nuclei in **3** are less well shielded than in any of the other 9-BBN oxalates and 9-BBN dicarboxylates described in this paper. This may be an indication that its structure may differ from all the others, and one alternative may be structure **3a** instead of **3**. Although there are two different kinds of environments for the boron atoms of compound **4**, only a

Table 1. Nuclear magnetic resonance data of 9-BBN dicarboxylates

	3[a]	4[a]	5[a]	6[b]	7[a]	8[b]
$\delta^{11}B$	29.3 (255)	17.6 (880)	52.3[a] 19.1[b]	8.5	17.7 (1420) 8.5 (280)	11.1 (1890)
$\delta^{13}C$	23.7 (C-3) 28.5 (C-1) 31.7 (C-2) 165.7 (C-4)	21.3 (C-1) 24.2 (C-6) 24.8 (C-3) 31.6 (C-2) 73.2 (C-5) 165 (C-4)	23.5 (C-3) 25.7 (C-1) 32.5 (b, C-2) 154.2 (C-4)	22.1 (C-1) 24.6 (C-3) 23.5 (C-3') 30.9 (C-4) 31.4 (C-4') 40.5 (C-4) 169.0 (C-6)	21.5 (b, C-1) 23.7 (C-3) 23.9 (C-3') 24.7 (C-2) 25.0 (C-2') 31.0 (C-2) 31.1 (C-2') 45.1 (C-4) 170.7 (C-6,6')	22.4 (C-1) 24.3 (C-3) 31.4 (C-2) 31.6 (C-4) 174.5 (C-5)

[a] In $CDCl_3$. – [b] In $[D_6]$DMSO.

single signal at comparatively high field is observed. This signal is quite broad [$h(1/2)$ = 880 Hz] indicating fluxional behavior as described in eq. (7). Fluxionality is also supported by the ^{1}H- and ^{13}C-NMR data which provide evidence for chemical equivalence of both 9-BBN groups. However, in the absence of any data for molecular masses in solution, the presence of oligomers in the solution cannot be excluded in a discussion. But any structure to be suggested must take into account that only three ^{13}C-NMR signals are found for the BBN units, e.g. the averaged structure in solution must be highly symmetrical.



Exchange reactions as described by eq. (7) were observed by Köster et al.[12] for a number of 9-BBN derivatives. The suggested structure for **4** is supported by a strong C=O stretching band at 1766 cm^{-1} in the IR spectrum of the solid. In contrast, compound **5** exhibit two ^{11}B-NMR signals. The intensity ratio of these signals is approximately 7:3 in $CDCl_3$ solution. However, only one signal should be present as suggested by the structural formula **5** which was verified by X-ray methods. The signal at δ = 52.3 corresponds to monomeric 9-BBN-OH[13] resulting from dissociation of this unit from **5**. The remaining molecule must be fluxional because only one ^{11}B-NMR signal is observed. Thus, the NMR data of compound **5**, which crystallizes from DME as a 1:1 solvate, are rather puzzling because the ^{1}H- and ^{13}C-NMR data indicate only one kind of 9-BBN unit as evidenced by only three signals for this group which must therefore reside in a highly symmetrical environment. This would be in accord with the suggested structure.

There are also tetracoordinated boron atoms present in compounds **6** to **8** as indicated by the respective ^{11}B resonances at $\delta \approx 10$. However, the simple structural formulae given for **6** to **8** cannot be correct as there is no evidence for uncoordinated C=O groups in the IR spectra of the solid compounds. Two bands in the region of 1600–1646 and 1570 to 1597 cm^{-1}, respectively, reveal that both oxygen atoms of the carbonyloxy group are involved in coordination. Consequently, the bis(9-BBN) dicarboxylates must be present as oligomers.

The boryl 2,2-dimethylmalonate **7** shows a single broad ^{11}B-NMR signal at δ = 17.7. More importantly, there are three pairs of ^{13}C-NMR signals for the 9-BBN group. These observations are not compatible with a structure as shown for **7** not only because an ^{11}B-NMR signal for a tricoordinated boron atom is missing in spite of the fact that a structure as depicted by **7** would be compatible with the ^{13}C-NMR data, but also if this structure was correct, we would expect three pairs of signals in a 1:1:2 ratio for the two 9-BBN units in the ^{13}C-NMR spectrum. However, all data are in accord with a tetrameric **7** as disclosed by its molecular structure as determined by X-ray methods.

NMR spectra for compounds **6** and **8** could only be recorded in dimethyl sulfoxide (DMSO) as solvent. This solvent most likely coordinates to the tricoordinated boron atoms (if there are any), and this would change the structure of these compounds. Consequently, no straightforward conclusion can be drawn as to the structures of these molecules in spite of the rather simple NMR spectra. The only additional structural information on the C(O)O group as provided by IR spectroscopy indicates that there is no uncoordinated C=O group, e.g. both oxygen atoms of the carbonyloxy unit coordinate to boron atoms. This definitely excludes monomeric structures. However, the degree of association for these compounds could neither be determind by cryoscopy (due to solubility problems) nor by mass spectrometry: The highest mass recorded stems from the fragment $(9\text{-BBN})_2O^+$, which is, however, not a diagnostic fragment. Therefore, the structures of the 9-BBN dicarboxylates had to be determined by X-ray crystallograpy. In spite of many efforts no single crystals of **3** could be grown but large

crystals of **4** were obtained from $CDCl_3$ solution which proved suitable for an X-ray structural determination. The result is depicted in Figure 2.

The basic structure of molecule **4** is a planar, five-membered 1,3,2-dioxa-borolan-4-one ring as part of a spirocyclic system. The 4-position of the dioxaborolane (as denoted in formula **4**) carries a 9-borabicyclo[3.3.1]nonyloxy moiety to which a THF molecule is firmly attached. There are two independent molecules in the unit cell which differ only slightly from one another except for the twist angles of the THF molecules.

Figure 2. ORTEP-type representation of one of the two independent molecules of **4**. Thermal ellipsoids are shown on a 25% probability scale. Esd's values are given in parenthesis. Selected bond lengths [Å]: B1–O3 1.586(9), B1–O4 1.536(8), B2–O2 1.578(8), B2–O5 1.555(9), C1–O1 1.197(7), C1–O4 1.290(7), C-2–O2 1.264(7), C2–O3 1.244(7), B1–C3 1.564(10), B1–C7 1.589(10), C1–C2 1.520(9), B2–C11 1.579(10), B2–C15 1.574(10). – Selected bond angles [°]: O4–B1–O3 98.4(5), O4–B1–C3 114.2(5), O4–B1–C7 112.2(6), O3–B1–C3 111.9(5), O3–B1–C7 109.3(5), C3–B1–C7 110.4(6), B1–O3–C2 109.7(5), O3–C2–C1 112.4(5), C2–C1–O4 106.5(5), C1–O4–B1 112.9(5), C2–C1–O1 125.5(6), O3–C2–O2 126.7(6), C2–O2–B2 126.5(5), O2–B2–O5 102.2(5), O2–B2–C15 115.0(5), O2–B2–C11 105.5(5), C11–B2–C15 108.9(6)

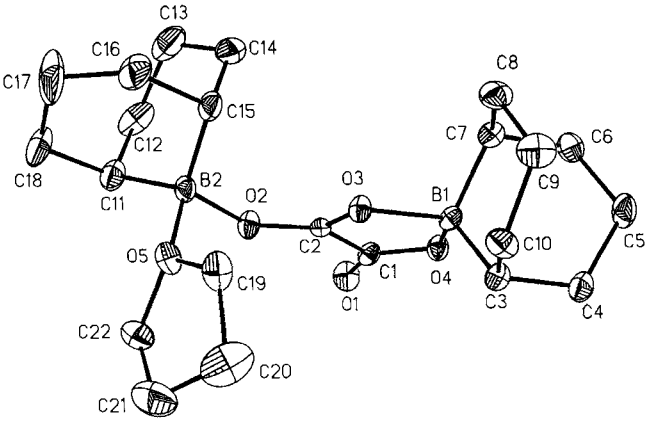
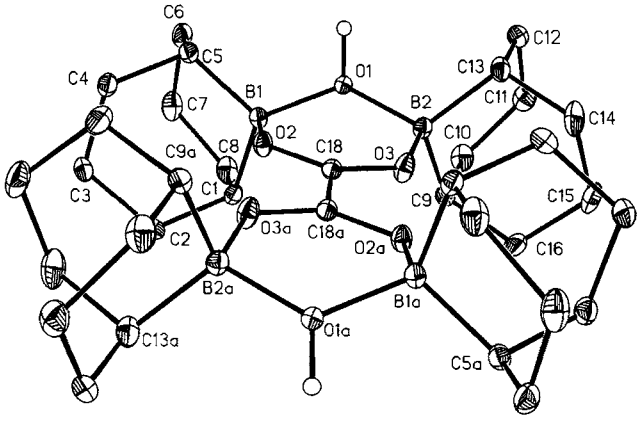


Figure 3. Molecular structure of **5** in ORTEP representation. Hydrogen atoms omitted except those of the OH groups. Thermal ellipsoids are drawn on a 25% probability scale. Selected bond lengths [Å]: B1–O2 1.578(2), B1–O1 1.532(2), O2–C18 1.245(2), O3–C18 1.249(2), B2–O3 1.581(2), B2–O1 1.535(2), C18–C18a 1.519(3). – Selected bond angles [°]: O1–B1–O2 103.7(1), B2–O1–C18 121.8(1), O2–C18–O3 127.9(1), C18–O3–B2 125.7(1), O3–B2–O1 103.5(1), B2–O1–B1 122.5(1), C1–B1–C5 108.7(1), C9–B2–C13 108.0(2), O2–C18–C18a 116.0(2)



The C–C bond of the oxalate unit in **4** corresponds to a single bond between sp^2-hydridized C atoms. Its carbon atoms are perfectly planarly coordinated. Electron density is more equally distributed in the O3–C2–O2 group than in the O4–C1–O1 unit, the terminal C1–O1 bond (1.196 Å) corresponds to a true C=O double bond. This brings more negative charge on atom O4 than on atom O3, and, consequently, the B1–O4 bond (1.54 Å) is shorter than the B1–O3 bond (1.59 Å), which can be considered a dative B–O bond. However, this would not comply with Haalands concept of dative bonds[14]. If the B1–O3 bond was a "true" dative bond then a bond length of >1.6 Å would be expected. However, the B2–O5 (1.56 Å) bond to the coordinated THF molecule is of almost the same length. Thus, **4** represents an example where covalent and coordinative B–O bond lengths do not differ significantly.

Internal bond angles at the carbon atoms of the five-membered ring closely match the ideal value for a regular pentagon while bond angles at the oxygen atoms are larger (110.3, 113.5°) and, consequently, a more acute angle is found at the boron atom (98.4°). The 9-BBN(THF)O group is almost perpendicular to the dioxaborolane ring plane of **4**.

The molecular structure of **5**, which crystallizes as **5** **DME**, is shown in Figure 3. In this case the oxalate dianion is coordinated to two formal $[(9\text{-BBN})_2OH]^+$ cations. An alternative description is that two 9-hydroxy-9-BBN molecules add to a bis(9-borabicyclo[3,3,1]nonyl) oxalate **3a** in such a manner that the boron atom of each of these units interacts with an oxygen atom of a different carbonyl unit of **3a**. The molecular skeleton of **5** adopts a crystallographically determined C_2 symmetry. The OH protons are, consequently, present in *trans* position to one another, and the six-membered B_2O_3C rings adopt a half-chair conformation.

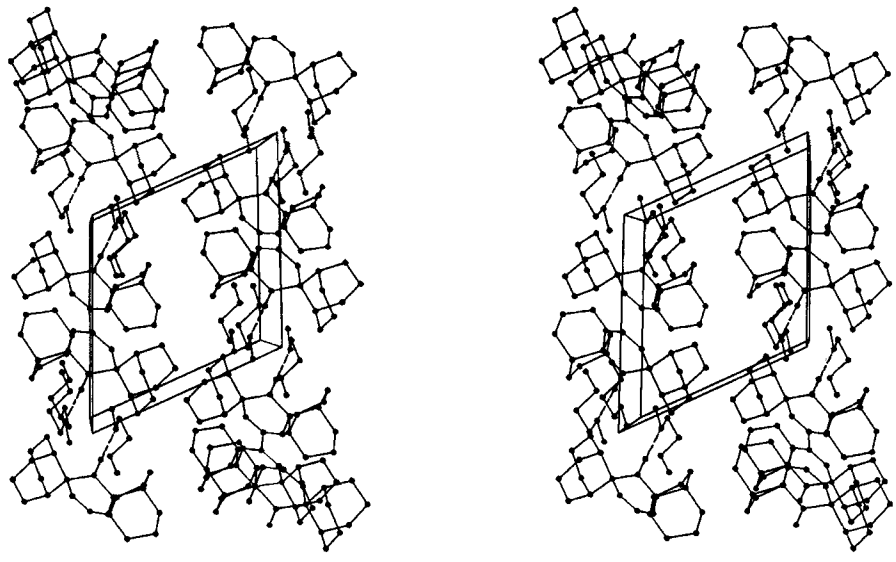
The C–O bonds in **5** are of equal length, and so are the B–O bonds to the carbonyloxy groups as well as those to the bridging OH groups. The latter are significantly longer than the former in spite of the fact that O1 is tricoordinated. All ring bond angles at the oxygen atoms are larger than 120°, the ideal angle for sp^2 hybridization, and this is especially noteworthy for atom O1 which cannot be regarded to be hybridized in such a way.

A symmetric charge distribution at the oxalate part of the molecule can be deduced from the structural features of **5**, and the $[9\text{-BBN}]_2OH^+$ cation is not only coordinated to the oxalate unit but also forms hydrogen bonds to the dimethoxyethane molecules in the crystal lattice as demonstrated in Figure 4.

Bis(9-BBN) 2,2-dimethylmalonate **7** crystallizes from $CHCl_3$ as the solvate $(\mathbf{7})_4 \cdot 1.75\ CHCl_3$ as determined by X-ray methods (see Figure 5, above).

The constituting monomeric unit of the tetramer is represented in Figure 5, below. It consists of a six-membered 1,3,2-dioxaborinane ring, and one of the two exocyclic O atoms carries a 9-BBN unit. This unit is jointed to the carbonyl oxygen atom of a neighboring monomeric unit via the tricoordinated boron atom. Linking of four of these

Figure 4. Stereoplot of the unit cell of **5** · **DME** showing the chains generated by hydrogen bridges (dashed lines) to DME molecules



units leads to the 32-membered ring system in $(7)_4$ which possesses a twofold axis running through atoms B1 and B4. However, the molecular symmetry of tetrameric **7** is close to point group D_2.

There are two kinds of carbonyloxy groups in tetrameric **7**. The first one shows equally long C–O bond lengths (average 1.26 Å) while the other C–O bonds are of different lengths (average 1.27 and 1.24 Å). Consequently, the B–O bond lengths to the shorter C–O bonds are longer than to the long C–O bonds. The former have, therefore, more carbonyl character than the latter, and delocalization of charge within the carbonyl groups is not uniform.

Reactions of Dicarboxylic Acids with Thexylborane

The results described so far demonstrate that the acyloxy function of carboxylic acids is not readily reduced by 9-BBNH. We assumed that this might also be true for monoorganylboranes as the reducing reagent. RBH_2 compounds that may be promising in this respect could be those with bulky groups R. For this reason we investigated reactions of thexylborane[15] with dicarboxylic acids in a 1:1 ratio, expecting hydrogen evolution and formation of heterocycles of type **9** as shown in eq. (8).

The reaction of thexylborane with oxalic acid in a 1:1 ratio in DME solution leads to an insoluble product that exhibits three ^{11}B resonance signals at δ = 55.7, 35.1, and 8.2 in $CDCl_3$ solution. Its solubility increases noticeably by adding a few drops of DMSO to the $CHCl_3$ solution, and under these conditions only a single resonance is observed, $\delta^{11}B$ = 8.2. If THF is used as the solvent, polymerization of THF affording a gel sets in at about −40 °C.

The same reaction in THF/DME but in a 2:1 ratio of thexylborane to oxalic acid reveals the formation of an intermediate as a THF (or DME) adduct. Reduction starts on heating the solution to 40 °C with formation of the bicyclic compound **10** which was isolated in 92% yield, eq. (9).

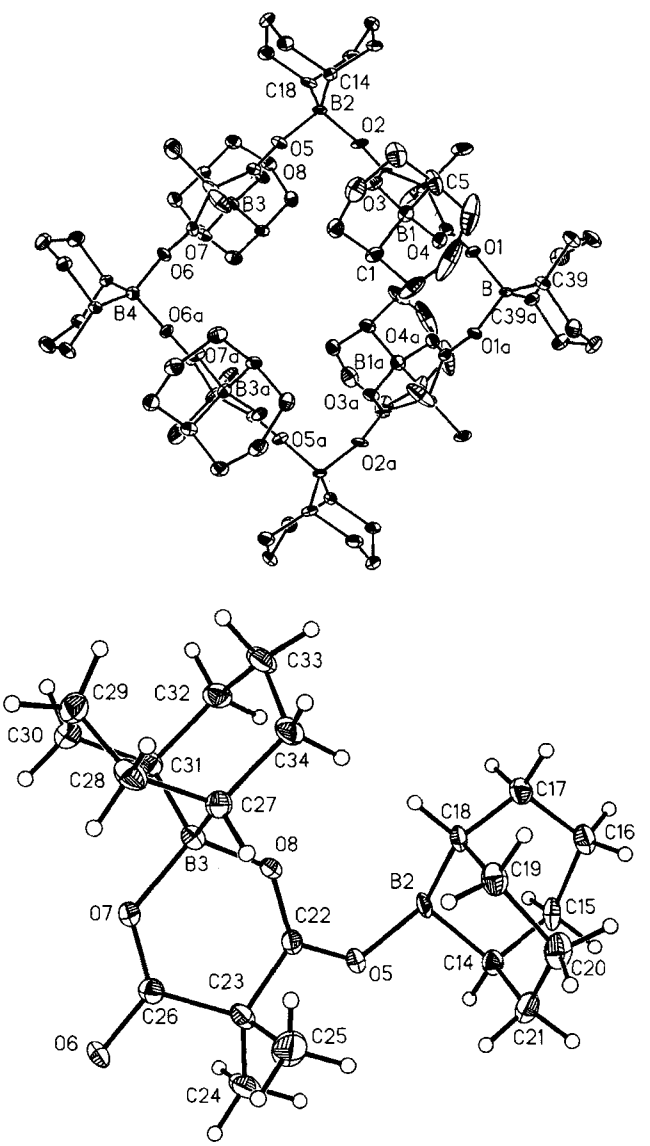
$\delta^{11}B$ = 36.5 for **10** is in accord with an alkyl-1,3,2-dioxaborolane ($\delta^{11}B$ = 34 to 40[17]). A structural alternative to **10** might be **10a** which cannot be excluded on the basis of the ^1H- and ^{13}C-NMR data, but if a four-membered ring system was present the ^{11}B nucleus would be more deshielded[16]. In addition, the molecular ion recorded for **10** in the mass spectrum decomposes with loss of CH_3, C_3H_8, and C_6H_{13}, leaving the $B_2O_4C_2$ unit intact. If **10** had a structure like **10a** then a cleavage of the central C–C bond should be observable in the mass spectrum. But this is not the case.

Malonic acid, 2,2-dimethylmalonic acid, and succinic acid behave like oxalic acid towards thexylborane; 1:1 reactions in THF lead to a species with tetracoordinated boron atoms ($\delta^{11}B$ = 12) as described e.g. for **10b** besides a tricoordinated borane ($\delta^{11}B$ = 51) whose chemical shift corresponds to an acyl-alkyl-hydroborane moiety[16] as shown by formula **10c**. The second equivalent of thexylborane does not reduce the carbonyl group of the primary reaction product at temperatures up to 60 °C. However, thexylboroxine $[Me_2HC–C(Me_2)BO]_3$ was isolated after the reactions were performed at temperatures above 80 °C. The mechanism by which this boroxine is formed has not yet been elucidated.

Reactions of Oxalic and 3,3-Dimethylmalonic Acid with BH_3 · THF and BH_3 · SMe_2

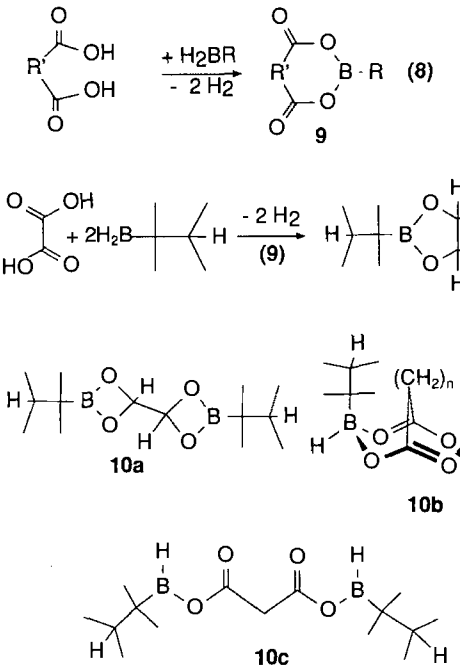
Monitoring the reaction of oxalic acid with BH_3 in THF is difficult for two reasons: 1) Oxalic acid is only very sparingly soluble in THF, thus preventing reactions under homogeneous conditions. 2) THF is rapidly polymerized[17]. However, polymerization is retarded or even suppressed at 0 °C, and this allows recording of ^{11}B-NMR spectra. Three signals are observed, a singlet at δ = 23.5, a doublet at δ = 28.9 [^1J(BH) = 176 Hz], and a doublet at δ = 6.6 [^1J(BH) = 155 Hz]. The doublet at δ = 28.9 is typical of an O_2BH structural unit. It would be in accord with a 1,3,2-dioxabo-

Figure 5. Above: ORTEP-type representation of the tetrameric molecule **7** in the crystal. Hydrogen atoms are omitted for clarity, and thermal ellipsoides are drawn on a 20% probability level. Only the framework atoms are numbered. Selected bond lengths [A]: B1–O3 1.52(1), B1–O4 1.57(1), B2–O2 1.57(1), B2–O5 1.55(1), B3–O7 1.56(1), B3–O8 1.56(1), B–O1 1.56(1), O1–C9 1.27(1), O2–C13 1.26(1), O3–C13 1.26(1), O4–C9 1.24(1), O5–C22 1.27(1), O6–C26 1.27(1), O7–C16 1.27(1), O7–C26 1.27(1), O8–C22 1.26(1), C9–C10 1.51(2), C10–C13 1.51(2), C22–C23 1.52(1), C23–C26 1.51(2). – Selected bond angles [°]: O1–B–O1a 105.0(11), O3–B1–O4 106.3(7), O2–B2–O 104.3(8), O7–B3–O8 104.8(7), O6–B4–O6a 105.2(10), B–O1–C9 129.5(6), B2–O2–C13 132.5(8), B1–O3–C13 125.3(8), B1–O4–C9 125.3(8), B2–O5–C22 130.0(7), B4–O6–C26 129.4(6), B3–O7–C26 126.0(8), B3–O8–C22 125.9(7), O1–C9–O4 122.4(10), O1–C9–C10 114.4(8), O4–C9–C10 123.1(9), O2–C13–C10 114.9(7).
Below: Plot of the monomeric unit of **7**

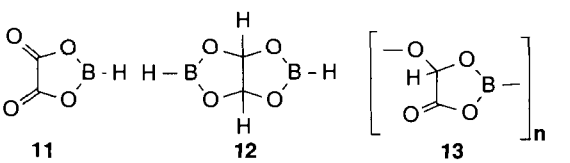


rolanedione structure **11** or with a structure of type **12**. The other doublet indicates the presence of a tetracoordinated boron atom, which most likely belongs to a BO_3H moiety. The signal that is less shielded may result from the coordination of a carbonyl oxygen atom to the O_2BH unit of either **11** or **12**, the other from THF addition. The resonance at $\delta = 23.2$ is indicative of the presence of **13** is solution.

Oxalic acid dissolves much better in DME as compared to THF. Therefore, we studied the reaction of this acid with $BH_3 \cdot SMe_2$ (ratio 1:2) at various temperatures by ^{11}B-NMR spectroscopy. The result is presented in Figure 6. It should be noted that not all of the borane–dimethyl sulfide reagent was consumed, and approximately 0.6 mol of the borane reagent did not react. This corresponds to a stoichiometry of acid to borane of approximately 2:3.

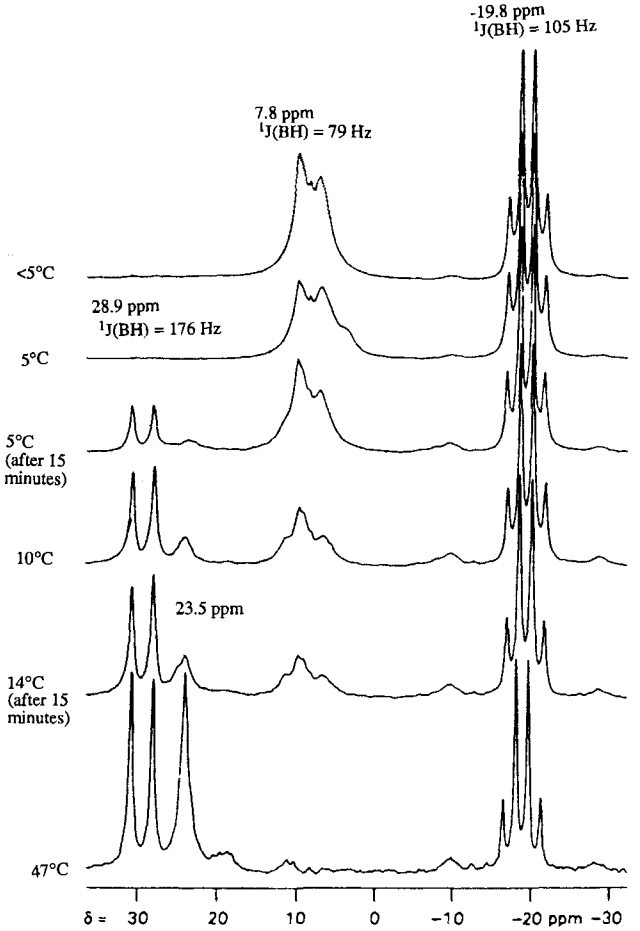


The reaction of oxalic acid with borane–dimethyl sulfide starts at about −10 °C, and two ^{11}B-NMR signals, a doublet at $\delta = 7.8$ and a singlet at 6.8, appear in the spectrum. The former could result from a Me_2S adduct of **11**. At temperatures >10 °C a doublet at $\delta^{11}B = 28.9$ emerges which we assign to the bicyclic dioxaborolane **12**. The singlet at $\delta^{11}B = 23.5$, the intensity of which increases as the reaction proceeds, indicates the presence of a BO_3 moiety where the boron atom is part of a dioxaborolane ring. This might be a compound of type **13**. Since we could not separate the products all assignments are speculative at the moment, and a more detailed study is warranted to explain the reaction sequences.



In contrast to oxalic acid we expected less complex reactions with 2,2-dimethylmalonic acid because both reagents are soluble in THF. Reactions start at about −40 °C as evidenced by the appearance of a shoulder at $\delta = 3.5$ emerging next to the signal of $BH_3 \cdot SMe_2$. As the reaction proceeds the intensity of the signal at $\delta = 24.9$ is rapidly gaining in

Figure 6. ^{11}B-NMR spectra (undecoupled) recorded during the reaction of oxalic acid with $BH_3 \cdot SMe_2$ in DME at various temperatures



intensity, and a singlet at $\delta = 17$ emerges and becomes the most prominent peak with raising temperature. After all $BH_3 \cdot SMe_2$ has been consumed, only the doublet at $\delta = 24.9$ and the singlet at $\delta = 17$ (ratio 3:7) remain. We assign the doublet to compound **14a** or **14b**. (It should be noted that **14b** contains two nonequivalent boron atoms. However, both are in a BO_2H environment. Therefore, the shielding should not be different, and only a single signal is to be expected in the ^{11}B-NMR experiment.) The singlet may be ascribed either to an alkoxyboroxine or, more likely, to the boric ester **15** because hydrolysis of the product yields 2,2-dimethyl-1,3-propanediol. Although the ^{11}B-NMR signal at $\delta = 3.5$ can be taken as evidence for the presence of a malonatoborane–THF adduct as the first product of the reaction, reduction proceeds quickly to the final products. Hydrolysis yields **16**.

Discussion

The present study of reactions of dicarboxylic acids with boranes clearly demonstrates that an efficient reduction of the acids to alcohols is only accomplished with $BH_3 \cdot THF$ and $BH_3 \cdot SMe_2$. With the latter reagents two boron-containing products are formed and characterized by ^{11}B-

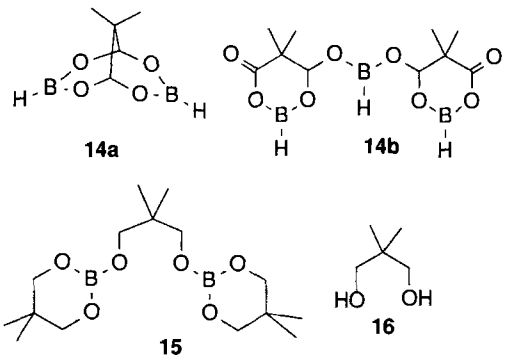
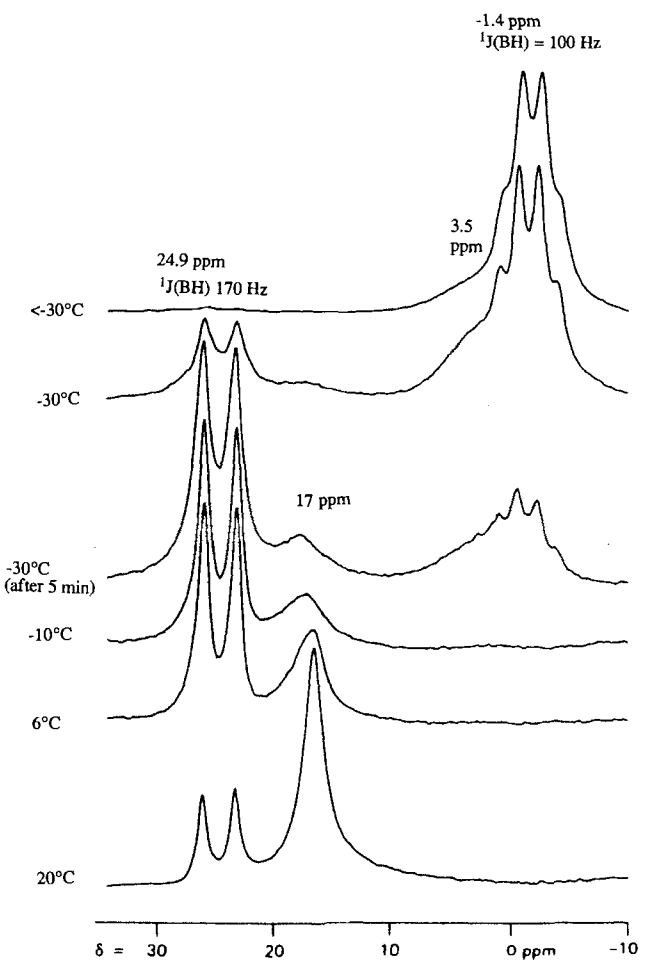


Figure 7. ^{11}B-NMR spectra (undecoupled) recorded during the reaction of 2,2-dimethylmalonic acid with $BH_3 \cdot SMe_2$ in THF at various temperatures



NMR spectroscopy as dialkoxyboranes and trialkoxyboranes, respectively.

The use of thexylborane as a less powerful reducing agent allows the detection of a dioxaborinanedione **9** or a bicyclic system such as **10b** as an intermediate, and these are formed rapidly with hydrogen evolution. Reduction of the carbonyl groups occurs in a second step, and in the case of oxalic acid a bicyclic 1,3,2-dioxaborolane **10** has been obtained. This reduction requires higher reaction temperatures. Thus, this reaction sequence differs from the sequence observed for the reaction of monocarboxylic acids with BH_3

THF[5], because the RC(O)OBH(R) unit formed is obviously sterically prevented from starting an intramolecular reduction. Consequently, a second borane molecule is necessary to achieve an intermolecular process.

No reduction occurs by allowing mono- and dicarboxylic acids to react with 9-BBNH as a model compound for diorganoboranes. 9-(Acyloxy)-9-BBN compounds are formed as demonstrated by Köster et al. for monocarboxylic acids[4]. These readily add THF or DMSO, and if no basic solvent is available they dimerize as proven by the X-ray structure determination of **2b** and **2c**. Thus, the acyl group enhances the Lewis acidity[4] of the boron atom in the 9-BBN derivatives reported here. More complex reactions occur between dicarboxylic acids and $(9\text{-BBNH})_2$, and the structure of the obtained products are also more complex. This is convincingly demonstrated for the product formed by the reaction of 9-BBNH with oxalic acid whereby new types of compounds, such as **4** and **5**, are generated and characterized by X-ray methods. If we consider the structural result for tetrameric dimethylmalonato-bis(9-borabicyclo[3.3.1]nonane) $(\mathbf{7})_4$ as a prototype for the products formed in the reactions of $(9\text{-BBNH})_2$ with malonic and succinic acids, then these should also not be present as monomers as described by the formulae **6** and **8**. It is not unlikely that they have structures similar to $(\mathbf{7})_4$ which features a 32-membered heterocycle.

Compounds formed by the reaction of dicarboxylic acids with monoorganoboranes probably exhibit a similarly complex structure. In the present work the 1,3,2-dioxaborolane-3,4-dione **9** is a likely intermediate en route to **10**. The corresponding *B*-methyl derivative was well characterized by Paetzold et al.[18] and was used for the gereration of MeB≡O[19]. Compounds of type **9** offer the perspective of being employed as useful RBO equivalents in synthesis.

Experimental

All experiments were conducted under anhydrous conditions in flame-dried Schlenk glassware or in a vacuum apparatus by using oxygen-free nitrogen or argon. Solvents were dried by standard procedures, distilled and stored under N_2. 9-BBN was prepared from $BH_3 \cdot THF$ and 1,5-cyclooctadiene[18]. $H_3B \cdot SMe_2$ was used as supplied by Aldrich, and the carboxylic acids were also commercial products. Dehydration of oxalic acid followed literature procedures[20]. – Elemental analyses: Microanalytical laboratory of the institute. – IR: Perkin-Elmer TF. – MS: Varian CH7 (70 eV); correct isotope patterns were observed for boron-containing fragments. – NMR: Jeol 270 (^1H, ^{13}C), Jeol 400 (^{13}C), Bruker AP 200 (^{11}B), standards: iTMS (^1H, ^{13}C), C_6D_6 (^{13}C), $BF_3 \cdot OEt_2$, (^{11}B); positive δ values refer to frequencies higher than the standard. – X-ray structural analysis: Siemens P4 or Nicolet R3m diffractometer, Mo-K_α radiation, graphite monochromator, SHELX Plus PC and SHELXL 93 programs for structure solution and refinement.

9-(Trifluoroacetoxy)-9-borabicyclo[3.3.1]nonane (**2a**): Trifluoroacetic acid (2.10 g, 18.4 mmol) was added dropwise to a stirred suspension of $(\mathbf{1})_2$ (2.25 g, 9.2 mmol) in 40 ml of dichloromethane. The mixture was allowed to warm up slowly, and most of $(\mathbf{1})_2$ went into solution at about 0 °C. Hydrogen evolution commenced at approximately 20 °C, while the solution turned yellow. Stirring was continued for about 12 h. Then the solvent was removed in vacuo leaving behind a brown oil that distilled a 25–30 °C/0.02 Torr to give a clear liquid. Yield: 3.86 g of **2a** (89%). The compound fumes heavily in contact with air and turns brown on standing at ambient temp. – NMR ($CHCl_3$): δ^1H = 0.97–2.0 (m). – $\delta^{11}B$ = 65.9 [*h*(1/2) = 530 Hz], in DMSO: 12.4 [*h*(1/2) = 1180 Hz). – $\delta^{13}C$ = 22.8 (C-3), 26.5 (C-1, broad), 33.6 (C-2), 114.4 [q, $^1J(^{19}F^{13}C)$ = 286 Hz, CF_3]; 155.7 [q, ^2J(FC) = 38 Hz, CO]. – $\delta^{19}F$ = –75.7. – IR [cm^{-1}]: 2988 w, 2925 s, 2848 m, 1975 s, 1766 m, 1227 s, 1159 s (CF_3). – MS *m/z*: 258 [$(9\text{-BBN})_2O^+$], 234 [$M^{\cdot+}$], 220 [M – CH_2^+], 140 [$FBC_8H_{14}^+$]. – $C_{10}H_{14}BF_3O_2$ (234.0): mass equivalent found: 229–232 by NaOH titration.

9-(Trifluoroacetoxy)-9-borabicyclo[3.3.1]nonane, Adduct with 1,2-Dimethoxyethane (2 **2a** · DME): Trifluoroacetic acid (2.54 g, 22.3 mmol) was added to a stirred solution of $(\mathbf{1})_2$ (2.72 g, 11.1 mmol) in 60 ml of DME at 0 °C. On allowing this mixture to attain ambient temp. hydrogen evolution started slowly and was complete (22 mmol) after stirring for 14 h. The solvent was then removed at 0.1 Torr. 6.19 g of (2 **2a**) · DME (99.5%) remained as a colorless solid. The compound sublimes at 40 °C/0.01 Torr and quite readily forms crystals up to the size of 1 cm. The complex is extremely moisture-sensitive, and its vapor pressure at 20 °C is high enough that the compound is carried away in a stream of nitrogen. Due to this high volatily its m.p. could not be determined in a sealed capillary. – NMR ($CDCl_3$): δ^1H = 1.26–1.86 (m, 28H, 9-BBN), 3.42 (s, 6H, MeO), 3.61 (s, 6H, CH_2O). – $\delta^{11}B$ = 47.2 [*h*(1/2) = 600 Hz)], in DME: 38.7 [*h*(1/2) = 355 Hz]. – $\delta^{13}C$ = 23.2 (C-3), 26.9 (br, C-1), 32.1 (C-2), 59.4 (OCH_3), 71.9 (OCH_2), 114.7 [q, $^1J(^{19}F^{13}C)$ = 286 Hz], CO not observed). – $\delta^{19}F$ = –75.3. – IR [cm^{-1}]: 2993 m, 2926 s, 2885 s, 2845 s, 2741 w, 2701 w, 2666 2, 2576, 1786 m, 1756 s, 1667 s (νCO), 1211 s, (νCF_3). – $C_{24}H_{38}B_2F_6O_6$ (558.2): mass equivalent found 555–557 by NaOH titration.

9-(Pivaloyloxy)-9-borabicyclo[3.3.1]nonane (**2c**): A solution of pivalic acid (3.05 g, 29.9 mmol) in 20 ml of DME was added dropwise to a stirred suspension of $(\mathbf{1})_2$ (3.64 g, 14.9 mmol) in 40 ml of DME. Hydrogen gas was liberated at about 30 °C. After the mixture had been kept for 2 d at 40 °C, all volatile components were evaporated at 20 °C/0.01 Torr leaving behind 6.57 g of pure **2c** (99%), m.p. 84 °C. Single crystals were grown by cooling slowly a hot saturated solution of **2c** in hexane to –50 °C. – MS, *m/z*: 351, 343 [$(9\text{-BBN})_2OC(O)CMe_3^+$], 222 [M/2$^+$], 194 [M/2 – CO]$^+$, 165, 138 [9-BBN – OH]$^+$. – $C_{13}H_{23}BO_2$ (222.1): calcd. C 70.29, H 10.44; found: C 69.44, H 10.36.

9-(Benzoyloxy)-9-borabicyclo[3.3.1]nonane (**2b**): A mixture of benzoic acid (2.70 g, 30.3 mmol) and $(\mathbf{1})_2$ (2.70 g, 15.2 mmol) in 40 ml of $CHCl_3$ was kept for 2 d at 60 °C. After this period a precipitate had formed which was isolated by filtration, washed with 5 ml of THF, and dried in vacuo. Yield: 2.18 g of **2b** (96.4%), m.p. 121–123 °C[4]. Single crystals were obtained by slow concentration of a $CHCl_3$ solution. Compound **2b** sublimes at 140 °C/0.01 Torr. – NMR (DMSO): δ^1H = 0.97 (br., s, 2H, 1-H), 1.45 (br., 4H, 3-H), 1.66 (br., 4H, 2-H), 1.76 (d, 4H, 2′-H), 7.46 (t, 2H, *m*-CH), 7.55, (t, 1H, *p*-CH), 7.98 (d, 2H, *o*-CH). – $\delta^{11}B$ = 12.9 [*h*(1/2) = 1230 Hz]; in $CDCl_3$: 32.5 (60%), 11.1 (30%), 3.6 (10%). – $\delta^{13}C$ = 24.5 (C-3), 22.6 (br., C-1), 31.6 (br., 2-C), 128.2 (*m*-C), 129.1 (*o*-C), 131.7 (*p*-C), 134.1 (*i*-C), 1676.6 (CO). – IR [cm^{-1}]: 1600, 1581 (νC=O). – MS, *m/z*: 258 [$(9\text{-BBN})_2O^+$], 242 [M$^+$], 217, 189, 147, 138 [9-BBN – OH]$^+$, 122 [9-BBN$^+$], 105 [$PhCO^+$], 77 [Ph$^+$]. – $C_{15}H_{19}BO_2$ (242.1): calcd. C 74.41, H 7.91; found: C 74.34, H 7.63.

9,9′-Oxalylbis(oxy)bis(9-borabicyclo[3.3.1]nonane) (**3**): A solution of oxalic acid (1.31 g, 14.6 mmol) in 50 ml of DME was added

dropwise with stirring to $(\mathbf{1})_2$ (3.56 g, 14.6 mol). Hydrogen gas started to develop at about 40°C. Gas evolution was completed after 24 h at 45°C. The oil remaining after the solvent had been evaporated solidified by adding 10 ml of dichloromethane. Yield: 4.78 g of **3** (98%) as an intensely yelow-colored microcrystalline powder. Purification was achieved by recrystallization from hot trichloromethane, m.p. 133°C (dec.). – NMR ($CDCl_3$): δ^1H = 0.73 (br., 4H, 1-H), 1.83 (br., 24H, 2,3-H). – IR [cm^{-1}]: 1706, 1660 (νCO). – $C_{18}H_{28}B_2O_4$ (330.0): calcd. C 65.52, H 8.55; found C 63.17, 8.20.

9,9'-Oxalylbis(oxy)bis(9-borabicyclo[3.3.1]nonane), Adduct with Tetrahydrofuran (**4**): A suspension of $(\mathbf{1})_2$ (3.03 g, 12.4 mmol) in 25 ml of DME and 20 ml of THF was added dropwise with stirring to a solution of oxalic acid (1.11 g, 12.4 mmol) in 20 ml of DME. A yellow solution formed as hydrogen evolution proceeded, and at the end of the reaction (20 h) a light yellow precipitate had separated which was isolated by filtration, washed with 3 ml of cold THF and then dried in vacuo. Yield: 4.2 g of **4** (93%), melting range 120–130°C (orange-colored at 100°C). Single crystals were obtained from dichloromethane solution. – NMR ($CDCl_3$): δ^1H = 0.49 (s, 2H, 1'-H), 1.09 (s, 2H, 1-H), 1.48 (br., 8H, 3-H), 1.71 (br., m, 16H, 2-H), 2.12 (s, 4H, THF), 4.43 (br., 4H, THF). – IR [cm^{-1}]: 1755, 1654 (νCO). – MS, *m/z*: 330 [M – THF]$^+$, 138 [9-BBN – OH]$^+$, 121 [9-BBN$^+$], 110 [$C_8H_{14}^+$]. – $C_{22}H_{36}B_2O_5$ (402.1): calcd. C 65.71, H 9.02; found C 65.14, H 8.81.

9,9'-Oxalylbis(oxy)bis(9-borabicyclo[3.3.1]nonane)Bis(9-hydroxy-9-borabicyclo[3.3.1]nonane), Adduct with 1,2-Dimethoxyethane (**5**): A solution of oxalic acid (0.47 g, 5.2 mmol) in 20 ml of DME was added to a suspension of $(\mathbf{1})_2$ (2.54 g, 10.4 mmol) in 25 ml of DME. Hydrogen evolution proceeded smoothly at 40°C, and a yellow suspension formed within 1 h. At this point water (1.9 ml) was added and the mixture heated at reflux with stirring. Yellow crystals separated from the solution on cooling to ambient temp. Yield 3.61 g of **5** (88%), m.p. 75–77°C. – NMR ($CDCl_3$): δ^1H = 0.97 (br., 8H, 1-H), 1.41 (br., 16H, 3-H), 1.79 (br., 32H, 2-H), 3.40 (s, 6H, OCH_3), 3.57 (s, 4H, OCH_2), 8.10 (br., 2H, OH). – IR [cm^{-1}]: 3219 m, 3115 m br, 2987 m, 2921 s, 2889 s, 2871 s, 2841 s, 2732 m, 2690 m, 2657 m, 2615 w, 1729, 1663 (νCO). – $C_{42}H_{78}B_4O_{10}$ (786.3): calcd. C 64.16, H 10.00; found C 63.25, H 9.98.

Bis(9-borabicyclo[3.3.1]non-9-yl)Malonate (**6**): Malonic acid (0.98 g, 9.45 mmol) and $(\mathbf{1})_2$ (2.31 g, 9.45 mmol) were suspended in 50 ml of DME with stirring. H_2 evolution proceeded slowly. A clear solution resulted after about 2/3 of the required volume of hydrogen gas (440 ml) had been liberated which was collected after a period of 14 h, and a colorless precipitate had formed which was isolated by filtration, washed with 10 ml of cold DME and dried in a vacuo. Yield: 3.15 g of **6** (97%); m.p. 216°C (dec.). Compound **6** is insoluble in pentane, benzene, toluene, and ether but slightly soluble in DME and diglyme, and easily in THF and DMSO. – NMR ([D_6]DMSO): δ^1H = 0.45 (br., 2H, 1-H), 0.73 (br., 2H, 1-H), 1.50, 1.63, 1.73 (m, 24H, 2,3-H), 3.00 (s, 2, 4-H). – IR [cm^{-1}]: 2981 m, 2949 m, 2886 s, 2864 s, 2841 s, 2691 w, 2659 w, 1646 s, 1597 s. – $C_{19}H_{30}B_2O_4$ (344.1): calcd. C 66.33, H 8.79; found C 65.49 H 8.78.

Bis(9-borabicyclo[3.3.1]non-9-yl) 2,2-Dimethylmalonate (**7**): Prepared in analogy to **6** from 2,2-dimethylmalonic acid (1.965 g, 14.9 mmol) and $(\mathbf{1})_2$ (3.63 g, 14.8 mmol) in 40 ml of DME. Quantitative formation of H_2 (705 ml). The suspension was quickly heated at reflux for 2 min and then cooled to 0°C. The precipitated product was isolated by filtration. Yield: 4.97 g of **7** (98%), m.p. 215–220°C (dec.). Single crystals were grown from $CHCl_3$ solution. – NMR ($CDCl_3$): δ^1H = 0.25 (br. 2H, 1-H), 0.58 (br, 2H, 1-H), 1.25 (s, 6H, 5-H), 1.32–1.52, 1.64, 1.78 (together 24H, 2,3-H). – IR [cm^{-1}]: 2983 m, 2935 s, 2895 s, 2689 w, 2661 w, 1708 m, 1631 s, 1596 s, 1213 s, 923 s, 761 st. – MS, recorded at 100°C, *m/z*: 372 [M$^+$, monomer], 258 [(9-BBN)$_2$O$^+$], 217, 148, 128 [9-BBN – OH]$^+$. Recorded at 100°C: 83, 85 [$CHCl_2^+$]. – $C_{21}H_{34}B_2O_4 \cdot CHCl_3$ (491.5): calcd. C 53.76, H 7.18; found C 53.57, H 7.30.

Bis(9-borabicyclo[3.3.1]non-9-yl) Succinate (**8**): Prepared in analogy to **6** from succinic acid (2.57 g, 21.8 mmol) and $(\mathbf{1})_2$ (5.3 g, 21.8 mmol). Hydrogen evolution ceased after 48 h at 40°C. The volume of the solution was then reduced to about 10 ml, and the solid that had formed was isolated by filtration, washed with ether (2 × 15 ml), and dried. Yield: 7.45 g of **8** (95.4%), m.p. 235°C (dec.). Compound **8** is soluble in hot THF or DMSO, but crystallization set in only after most of the solvent had been removed. – NMR ([D_6]DMSO): δ^1H = 0.79 (br., s, 2H, 1-H), 1.39, 1.56, 1.66 (all br., together 24H, 2,3-H), 2.36 (s, 4H, 4-H). – MS, *m/z*: 359 [M$^+$], 258 [(9-BBN)$_2$O$^+$], 152, 138 [9-BBN – OH]$^+$, 110 [$C_6H_{14}^+$]. – $C_{20}H_{32}B_2O_4$ (358.1): calcd. C 67.08, H 9.01; found C 67.11, H 8.59.

3a,6a-Dihydro-2,5-bis(1,1,2-trimethylpropyl)-1,3,2-dioxaborolo-[4,5-d]-1,3,2-dioxaborole (**10**): 2,3-Dimethyl-2-butene (6.94 g, 82.5 mmol) was added at 0°C with stirring to a solution of BH_3 in THF (39.2 ml, 82.5 mmol). After 1 h a solution of oxalic acid (3.71 g, 41.2 mmol) in 100 ml of DME was added. Hydrogen evolution started, and 80 mmol of gas was collected within 5 h. The mixture was then kept for 8 h at reflux. After this period the solvent was removed in vacuo and the residue subjected to fractional distillation to afford **10** as a colorless liquid, b.p. 90–100°C/0.01 Torr, which solidified on standing, m.p. 30°C. Yield: 10.7 g of **10** (92%). – NMR ($CDCl_3$): δ^1H = 0.85 (d, 1H, 4-H), 0.93 (s, 12H, 5-H), 1.64 (sept., 2H, 3-H), 5.97 (s, 2H, 1-H). – $\delta^{11}B$ = 36.5 [*h*(1/2) = 400 Hz]. – $\delta^{13}C$ = 18.4 (m, C-4), 21.1 (m, C-5), 23.7 (br., C-2), 34.6 (m, C-3), 102.3 [dd, C-1, ^1J(CH) = 175.1, ^2J(CH) = 9.5 Hz]. – IR (cm^{-1}, neat liquid): 2960 s, 2937 s, 1474 s, 1396 s, 1371 s, 1306 m, 1278 w, 1217 s, 1172 m, 1125 s, 1122 s, 1091 s, 1072 m. – MS, *m/z* (%): 282 (10) [M$^+$], 267 (20) [M – Me]$^+$, 240 (100) [M – C_3H_6]$^+$, 192, 128, 112 (10) [$HBO_2C_2O_2BH^+$], 85 [$C_6H_{13}H^+$], 84 [$C_6H_{12}^+$], 83 [$C_6H_{12}^+$], 69 [$C_5H_5^+$]. – $C_{14}H_{28}B_2O_4$ (282.0): calcd. C 59.63, H 10.01; found C 59.72, H 9.81.

Reactions of Dicarboxylic Acids with Thexylborane: Isolation of Thexylboroxine: The dicarboxylic acids were added to a solution of two equivalents of freshly prepared thexylborane[21] in THF with stirring. After hydrogen evolution had ceased ^{11}B-NMR spectra were recorded from the solution (vide infra). Then the solution was heated at reflux. The oily product which remained after evaporation of the solvent in vacuo could not be crystallized from a varity of solvents. Distillation yielded thexylboroxine, b.p. 85–87°C/0.02 Torr. Yields were not determined. Thexylboroxine was also prepared by hydrolysis of thexylborane. – ^{11}B-NMR results [given in the order for thexyl(RO)BH, thexylB(OR)$_2$, thexyl(RO)BH · THF, thexylBH$_2$]: 2,2-Dimethylmalonic acid: 51.8 (30%), 32.6 (s, 45%), 11.8 (br, 4%), 24.1 (m, 21%). – Succinic acid: 51.7 (d, 132 Hz, 10%), 32.4 (s, 50%), 12.2 (br., 10%), 24.1 (m, 30%). – Phthalic acid: 51.3 (br., 30%), 32.0 (s, 40%), 4.0 (br. 5%), 24.1 (m, 20%). – NMR data for thexylboroxine in $CDCl_3$: δ^1H = 0.82 [d, ^1J(HH) = 6.8 Hz, 18H, 3-H], 0.89 (s, 18H, 4-H), 1.65 (sept, 3H, 2-H). – $\delta^{11}B$ = 33.9. – $\delta^{13}C$ = 18.5 (C-5), 21.0 (C-4), 26.4 (C-1), 34.30 (C-2). – MS, *m/z* (%): 336 (5) [M$^+$], 321 (63) [M – Me]$^+$, 293 (60) [M – C_3H_7]$^+$, 277 (32), 250 (45), 148 (43), 84 (80) [$C_6H_{12}^+$], 44 (100) [$C_3H_8^+$]. – $C_{18}H_{26}B_3O_3$ (335.9): calcd. C 64.36, 11.70; found C 62.81 H 11.07.

Reduction of 2,2-Dimethylmalonic Acid with BH_3 · THF: 2,2-Dimethylmalonic acid (0.66 g, 5 mmol) was added at –78°C to 14.6

Table 2. Crystallographic data of **2b**, **2c**, **5**, and **7** as well as data concerning data collection and refinement of the structures

	2b	2c	4	5	7
Formula	$C_{15}H_{19}BO_2$	$C_{13}H_{23}BO_2$	$C_{22}H_{35}B_2O_5$	$C_{42}H_{78}B_4O_{10}$	$C_{21}H_{34}B_2O_4 \cdot 1.75\ CHCl_3$
Mol. wght.	242.1	222.1	401.1	786.3	479.7
a [Å]	6.483(2)	11.91(1)	14.28(1)	10.094(2)	18.293(6)
b [Å]	9.198(3)	14.58(1)	12.336(7)	10.921(4)	25.949(5)
c [Å]	11.815(3)	15.394(9)	25.24(2)	11.148(3)	21.992(5)
α[°]	102.67(2)	90	90	77.37(2)	90
β[°]	111.41(2)	90	96.90(6)	87.94(1)	100.93(4)
γ[°]	90.230(2)	90	90	65.94(2)	90
V [Å^3]	637.2(4)	2874(5)	4413(6)	1093.0(5)	10250(5)
Z	2	8	8	1	16
space group	P1bar	$C222_1$	$P2_1/c$	P1bar	C2/c
$d_{calc.}$ [g/cm^3]	1.262	1.104	1.207	1.195	1.243
μ [cm^{-1}]	0.8	0.7	0.82	0.81	3.53
F(000)	260	976	1736	430	4065
cryst.size[mm]	.33x.5x.5	.3x.4x.52	.4x.5x.5	.35x.47x.5	.35x.4x.56
T (K)	223	173	228	173	173
scanspeed[°/min]	2.8-60	3.1-60	3.2-60	2.0-60	2.9-60
2Θ-range	2 - 46	4.4-45	3.0-47	2 - 47	3 - 47
refl. measured	2243	1921	5889	3813	5937
refl. unique	1702	1637	5450	3190	5445
refl. observed	1396 (4σ)	1246	3068(3σ)	2609	3514
R_1	0.038	0.058	0.084	0.040	0.100
R_w	0.048	0.080	0.158	0.051	0.129
GOOF	1.058	1.05	1.07	1.054	3.03
No. variables	220	213	523	253	555
Δe [e/Å^3]	0.14	0.25	0.33	0.21	1.2

ml of a BH_3 solution in THF (10 mmol of BH_3). From a sample ^{11}B-NMR spectra were recorded at several temperatures after the acid had dissolved (see Figure 6). A total of 220 ml of hydrogen gas was collected after the solution had attained ambient temp. The solvent was then evaporated, the residue hydrolyzed, and the mixture was extracted with ether. Distillation of the ether phase from the extract yielded 0.32 g (61%) of 2,2-dimethyl-1,3-propanediol (b.p. 123–126°C).

Reduction of Oxalic Acid with $BH_3 \cdot SMe_2$: Oxalic acid (0.82 g, 9.1 mmol) and $H_3B \cdot SMe_2$ (1.38 g, 18.2 mmol) were added to 15 ml of DME at −78°C. A sample was taken for recording the ^{11}B-NMR spectra (see Figure 6). On warming to ambient temp. a total of 400 ml of hydrogen gas was formed (18 mmol), and a colorless product precipitated. This was isolated and hydrolyzed. The product shows signals assigned to oxalic acid ($\delta^{13}C$ = 160.4) and ethylene glycol ($\delta^{13}C$ = 67.2) in the ^{13}C-NMR spectrum.

Crystal Structure Determinations: The selected single crystals were mounted in glass capillaries under argon. Cell parameters were determined from the setting angles of 18 to 30 reflections, and the Laue symmetry was determined by measuring the intensities of symmetry-related reflections. Some details of the X-ray structural determinations are summarized in Table 2. All structures were solved by direct methods, and the model was refined by difference Fourier synthesis and FMLS calculations. Nonhydrogen atoms were refined with anisotropic temperature parameters and H atoms in found positions with fixed isotropic U_i. No other constraints were allowed. The site occupation factors for the $CHCl_3$ molecules in **7** were refined freely but kept fixed in the final stage of the refinement. One of the two solvent molecules seems to be disordered leaving fairly large residual electron density in close vicinity of the chlorine atoms.

Further details of the X-ray structure determination are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, and can be obtained by quoting the depository numbers CSD-401620–401624, the name of the authors, and the literature citation.

☆ Dedicated to Prof. Dr. *A. Schmidpeter* on the occasion of his 65th birthday.

[1] P. Kölle, H. Nöth, H. Stolpmann, M. Thomann, *Chem. Ber.* **1995**, *128*, 205–212.

[2] L. H. Toporcer, R. E. Dessy, S. I. E. Green, *Inorg. Chem.* **1965**, *4*, 1644–1655; *J. Am. Chem. Soc.* **1965**, *87*, 1236–1240; E. Rothgery, R. Köster, *Liebigs Ann. Chem.* **1974**, 101–111.

[3] R. Köster, *Liebigs Ann. Chem.* **1974**, 101–111.

[4] M. Yalpani, R. Boese, K. Seevogel, R. Köster, *J. Chem. Soc., Dalton Trans.* **1993**, 47–50, and literature cited therein.

[5] H. C. Brown, P. Heim, N. M. Moon, *J. Am. Chem. Soc.* **1970**, *92*, 1637–1646.

[6] C. F. Lane, *Chem. Rev.* **1976**, *76*, 773–799.

[7] H. C. Brown, T. P. Stocky, *J. Am. Chem. Soc.* **1977**, *99*, 8218–8226.

[8] R. Contreras, B. Wrackmeyer, *Z. Naturforsch, Teil B*, **1980**, *35*, 1237–1240.
[9] The crystal structure of **2b** has been determined also by Köster et al.[4]. Our data are fully compatible with those reported. Therefore, we will neither depict its molecular structure nor its bonding parameters although the *R* factor of our data is slightly smaller.
[10] S. H. Bauer, J. Y. Beach, *J. Am. Chem. Soc.* **1941**, *63*, 1394–1399; W. Zachariasen, *Acta Crystallogr.* **1954**, *7*, 305.
[11] C. P. Brook, R. P. Minton, K. Niedenzu, *Acta Crystallogr., Sect. C*, **1988**, *43*, 207–212; H. Nöth, G. Geisberger, *Chem. Ber.* **1990**, *123*, 953–964.
[12] R. Köster, G. Seidel, K. Wagner, B. Wrackmeyer, *Chem. Ber.* **1993**, *126*, 305–317.
[13] Private communication of R. Köster to A. Lang.
[14] A. Haaland, *Angew. Chem.* **1989**, *101*, 1017–1032; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992–1007.
[15] G. Zweifel, H. C. Brown, *J. Am. Chem. Soc.* **1963**, *85*, 2066.
[16] H Nöth, B. Wrackmeyer, *NMR Spectroscopy of Boron Compounds*, vol. 14 of *NMR: Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer Verlag, Berlin, Heidelberg, New York, **1978**.
[17] R. Köster, P. Binger, *Inorg. Synthesis* **1974**, *15*, 141–145; H. C. Brown, *Organic Synthesis via Boranes*, J. Wiley and Sons, New York, London, **1975**.
[18] P. Paetzold, P. Bohm, A. Richter, E. Scholl, *Z. Naturforsch., Teil B*, **1967**, *31*, 754–764.
[19] H. Bock, L. S. Cederbaum, W. von Niessen, P. Paetzold, P. Rosmus, B. Solouki, *Angew. Chem.* **1989**, *101*, 77–78; *Angew. Chem. Int. Ed. Engl.* **1989**, 88–89.
[20] E. Negishi, H. C. Brown, *Synthesis* **1974**, 77–89.

[95021]